JOURNAL OF SPACECRAFT AND ROCKETS
Vol. 43, No. 2, March–April 2006

Influence of UV Radiation on Outgassing of Polymeric Composites

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Aspects concerning influence of UV radiation on outgassing processes in vacuum for acrylic copolymer-based composites are discussed. Mathematical models describing the outgassing processes in materials being subjected to UV radiation as well as deposition of emerged volatile products are given. Comparative analysis of experimental results of UV action on outgassing kinetics for materials with different filler/binder ratios at different temperatures is carried out.

Nomenclature

A_{i0} = parameter that depends on composition of material under test and UV source
a_{i0} = parameter defining influence of UV radiation on desorption kinetics of i component
$C_i(h-\upsilon t, t)$ = concentration of i-type volatile products in the near-surface layer of material
$C_i(x,t)$ = concentration of i component of outgassing process in material
D_i = effective coefficient of diffusion of i component
$F_i(t)$ = dependence of flux of i component emitted from material through the unit of surface on time t
h = thickness of material
k_{ci} = effective coefficient of remission of i component from the surface element
k_i = effective coefficients of desorption of i component
k_i^+ = effective desorption coefficient of i-type "heavy" component
$M_{\text{ci}}(t)$ = dependence of mass of i component deposited on a condensation surface element on time t
$M_{\text{si}}(t)$ = dependence of mass of i component in sample on time t
R_i = concentration of i component in material at initial moment
$S_i^+(t)$ = source function of i-type "heavy" component in the near-surface layer of material determined by influence of UV radiation on material.
S_0 = surface area of sample
α^{photo} = effective coefficient of linear reduction of UV radiation
α_{cs} = geometrical factor that depends on arrangement of volatile products source with respect to the condensation surface
β_i = effective first-order reaction rate with i component
$\delta M_s(t)$ = time dependence of a sample mass loss
λ_k = characterictic value of differential equation
$\sigma_{i\to m}^{\text{photo}}$ = weighting coefficient of photodestruction of i-type component through j channel
υ = evaporation rate of material
χ_{ci} = chemical reaction rates with involvement of i component on condensation surface
χ_i = chemical reaction rates with involvement of i component

Introduction

OUTGASSING of a polymeric composite subjected to ultraviolet (UV) radiation in vacuum involves the following basic processes: desorption of volatile products (VP) adsorbed or generated on the surface of material; and diffusion and desorption of gaseous substances adsorbed by material or generated in it as well as evaporation of material as a result of UV radiation.

When polymeric composites are under exposure to solar radiation, increase of outgassing rate as a result of photodecomposition of polymeric components is determined mainly by the UV part of solar spectrum. This is stipulated by a number of features of the photochemical processes that occur in materials under exposure to UV and that the major part of VUV radiation is absorbed by the thin near-surface layer of material. The latter can cause the "heavy" in mass but easily surface-condensable VP to be moved from the thin layer of a polymeric composite into the gaseous phase.

Outgassing and Condensation Model

To describe mathematically the influence of UV on physical and chemical processes that occur in a material and on its surface, we have made use of principal postulates accepted in the model of outgassing at thermal-vacuum action.[1,2] The change of concentration of outgassing components in a material applied to a hermetically enclosed substrate is stipulated by the following processes: desorption from the surface at the material-vacuum boundary; photodestruction of the material; chemical reactions; evaporation of the material; and diffusion resulting from the aforesaid processes.

Mathematical models of outgassing processes in composites use effective coefficients, that is, parameters describing the processes that take place in laboratory and onboard experiments.

Under these assumptions, the change of concentration of i-type outgassing component $C_i(x,t)(i = 1, 2, 3 \ldots N)$ in material being in vacuum under exposure to UV radiation can be described by the following differential equations:

$$\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C_i(x,t)}{\partial x^2} - \left(\sum_{m=1}^{M} \sigma_{i\to m}^{\text{photo}} + \chi_i\right) C_i(x,t) + A_{i0}\exp[\alpha^{\text{photo}}\cdot(x+\upsilon\cdot t-h)]$$

$$x\in(0,h-\upsilon\cdot t), \qquad t>0 \quad (1)$$

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that satisfy the initial and boundary conditions:

$$C_i(x,t)|_{t=0} = R_i, \qquad x \in [0, h] \tag{2}$$

$$D_i \frac{\partial C_i(x,t)}{\partial x}\bigg|_{x=h-\upsilon\cdot t} + (k_i + a_{i0}) C_i(x,t)|_{x=h-\upsilon\cdot t} = 0$$

$$\frac{\partial C_i(x,t)}{\partial x}\bigg|_{x=0} = 0, \qquad t > 0 \tag{3}$$

The heavy outgassing components are not able to diffuse over material. Therefore it is sufficient to examine the dynamics of change of their concentrations in the near-surface layer ($x = h - \upsilon t$), which can be described by the following equation:

$$\frac{\mathrm{d}C_i^+(h-\upsilon\cdot t, t)}{\mathrm{d}t} = -k_i^+ C_i^+(h-\upsilon\cdot t, t) + S_i^+(t)$$

$$C_i^+(h-\upsilon\cdot t, t)|_{t=0} = R_i \tag{4}$$

Functions $C_i(x,t)$ obtained while solving Eqs. (1–3) with $\sigma_{i\to m}^{\text{photo}}$ weighting coefficients can enter the equations describing the changes of concentration of m-type outgassing component ($m = 1, 2, 3 \ldots M$) that could be generated in the course of destruction of proper i-type component. Searching in such a way all feasible outgassing components, one can create a system of equations describing changes of their concentrations in the material.

To study outgassing in vacuum, quartz microbalances that convert the changes of mass added onto the quartz piezoresonator surface into alteration of output frequency of self-oscillator are used. Thus, the outgassing process is monitored by observing the deposition of VP onto the surface of the sensitive mass loss sensor. Therefore, to interpret the experimental data we have to introduce the model that binds the mass loss rate $\mathrm{d}M_{\text{si}}(t)/\mathrm{d}t$ and the deposition rate of part of this mass $\mathrm{d}M_{\text{ci}}(t)/\mathrm{d}t$ on the condensation surface.

The latter can cause the heavy in mass but easily surface-condensable VP to be moved from the thin layer of a polymeric composite into the gaseous phase:

$$\frac{\mathrm{d}M_{\text{si}}(t)}{\mathrm{d}t} = -(\upsilon + k_i + a_{i0}) S_0 C_i(h - \upsilon t, t) \tag{5}$$

$$\frac{\mathrm{d}M_{\text{ci}}(t)}{\mathrm{d}t} = \frac{-\alpha_{\text{cs}}\,\mathrm{d}M_{\text{si}}(t)}{\mathrm{d}t} - k_{\text{ci}} M_{\text{ci}}(t) - \chi_{\text{ci}} M_{\text{ci}}(t) \tag{6}$$

As for the laboratory experiments on VP outgassing and deposition where alterations in thickness of VP source can be neglected, solution of the system (5) and (6) for $M_{\text{ci}}(t)$ has the following form:

$$M_{\text{ci}}(t) = \alpha_{\text{cs}} S_0 k_i^* \sum_{n=1}^{\infty} \left\{ \frac{f_n - g_n}{\eta_{\text{ci}} - b_i} [\exp(-b_i t) - \exp(-\eta_{\text{ci}} t)] + \frac{g_n}{k_{\text{ci}}} [1 - \exp(-\eta_{\text{ci}} t)] \right\} \tag{7}$$

where

$$f_n = \frac{2R_i}{1 + h\left(k_i^*/D_i + \lambda_n^2 D_i / k_i^*\right)}, \qquad tg\lambda_n h = \frac{k_i^*}{\lambda_n D_i}$$

$$g_n = A_0 \frac{\lambda_n \sin 2\lambda_n h + 2\alpha^{\text{photo}} \cdot \cos\lambda_n h \left[\cos\lambda_n h - \exp(-\alpha^{\text{photo}} \cdot h)\right]}{h \cdot \left(\alpha^{\text{photo}2} + \lambda_n^2\right) \cdot b_i}$$

$$b_i = \lambda_n^2 D_i + \beta_i, \qquad \beta_i = \sum_{m=0}^{M} \sigma_{i\to m}^{\text{photo}} + \chi_i$$

$$\eta_{\text{ci}} = k_{\text{ci}} + \chi_{\text{ci}}, \qquad k_i^* = k_i + a_{i0} \tag{8}$$

Weight of the i-type outgassing heavy component $M_{\text{ci}}(t)$ deposited on the unit condensation surface by time t, which was found when solving the system (5) and (6), is

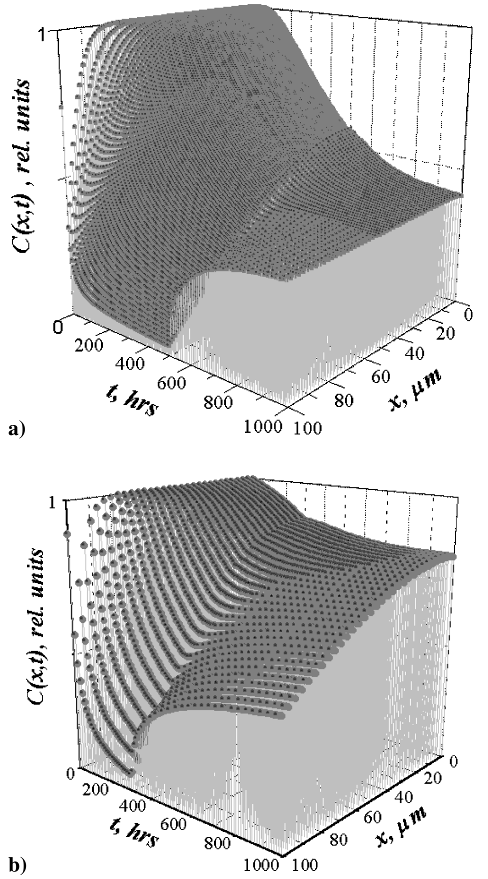

Fig. 1 Distribution of VP in polymeric composite: a) stepwise reduction of outgassing rate and b) action of highly intensive UV radiation.

$$M_{\text{ci}}(t) = \left\{ M_{\text{ci}}(0) + \alpha_{\text{cs}} S_0 k_i^+ \int_0^t \exp\left[\left(\eta_{\text{ci}} - k_i^+\right)\tau\right] \cdot \left[R_i^+ + \int_0^\tau S_i^+(\xi) \exp\left(k_i^+ \xi\right) \mathrm{d}\xi \right] \mathrm{d}\tau \right\} \exp(-\eta_c t) \tag{9}$$

The outgassing rate of VP source and deposition and reemission rates on/from the condensation surface, respectively, are defined mainly by the constants in Eqs. (7–9).

Results of Numerical Computation and Discussion

Figure 1 shows curves of VP concentration changes for stepwise reduction of outgassing rate (Fig. 1a) and UV source activation (Fig. 1b) at $t = 400$ h. The first event can occur if the material is withdrawn from the vacuum chamber. In this case, distribution of VP concentration in material became even with time.

Curve 1b shows VP concentration changes in material when the volume VP absorption takes place. Here is realized the opportunity that refers to a small value of the parameter α^{photo} at highly intensive UV radiation (great values of the parameters A_{i0}); therefore, one can observe the growth of VP concentrations both in the near-surface layers and in volume of the material. The curves of Fig. 1 are for illustration of the VP concentration changes in material only.

Experimental Results

The DDS-30 deuterium lamp with spectral density shown in Fig. 2 was used as the source of UV radiation. This lamp was mounted inside the vacuum chamber so that the uniform influence over the whole sample surface of the VP source material was achieved. Figure 3 shows schematic diagram of the “Vesy” equipment that

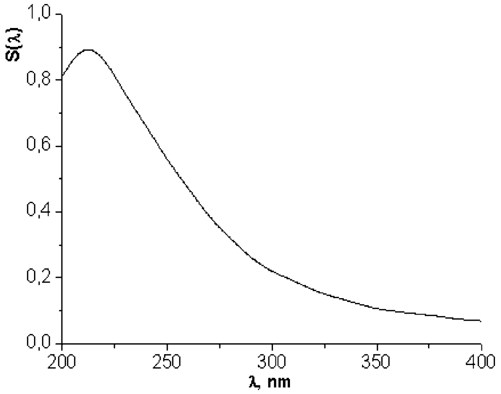

Fig. 2 Spectral density of the source of UV radiation.

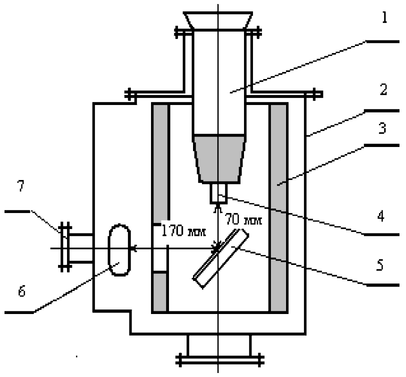

Fig. 3 Schematic diagram of the Vesy equipment: 1, reservoir that is filled in with liquid nitrogen to control thermostatically the mass flow sensor; 2, vacuum chamber body; 3, cryogenic shield; 4, mass flow sensor; 5, heating table with sample; 6, UV sources; and 7, quartz window.

was used to study influence of UV radiation on outgassing kinetics at different sample temperatures.

To determine the outgassing rates of materials in vacuum, we have used the quartz microbalance with the 10-MHz AT-cut mass-sensitive piezoresonator thermally stabilized at (82 ± 5)°K. A sample was attached to the table in the vacuum chamber. Experiments were carried on at pressure of no greater than $(2 \pm 0.5) \times 10^{-4}$ Pa. Experimental results of influence of UV radiation on outgassing of polymeric composites are given in Fig. 4. Data processing shows that outgassing rate in polymeric materials under exposure to UV radiation depends on both the temperature and the polymeric binder/filler (ZnO as binder and acrylic copolymer as filler in our case) volume ratio. Figures 4a and 4b present polymeric binder/filler volume ratios of 1:0 and 1:1, respectively.

Figure 4c shows experimental data of EKOM-1 thermal coating[3] mass loss caused by outgassing process. Both samples prior to $t = 8$ h are subjected to thermal-vacuum action. Then one of them was subjected to UV radiation (curve 2), which led to a significant increase of mass loss in the outgassing process as compared to mass loss (curve 1) of the sample that was not exposed to UV radiation. Finally, Fig. 4d gives the kinetics of the sample mass loss for the experiment that coincides with previous ones during the first 22 h; thereafter, the sample temperature was maintained at 125°C, and then, at $t = 25$ h, UV radiation was activated.

Conclusions

The results of numerical calculations of the outgassing process when polymeric composites are subjected to UV radiation show a significant dependence of the amount of VP emerged from the exposed materials under study both on the basic parameters characterizing the material itself and on the emission source spectrum.

The experimental data show that the outgassing rate depends on the temperature of the material and the volume ratio of the polymeric binder/filling agent in the case when polymeric materials are subjected to UV radiation.

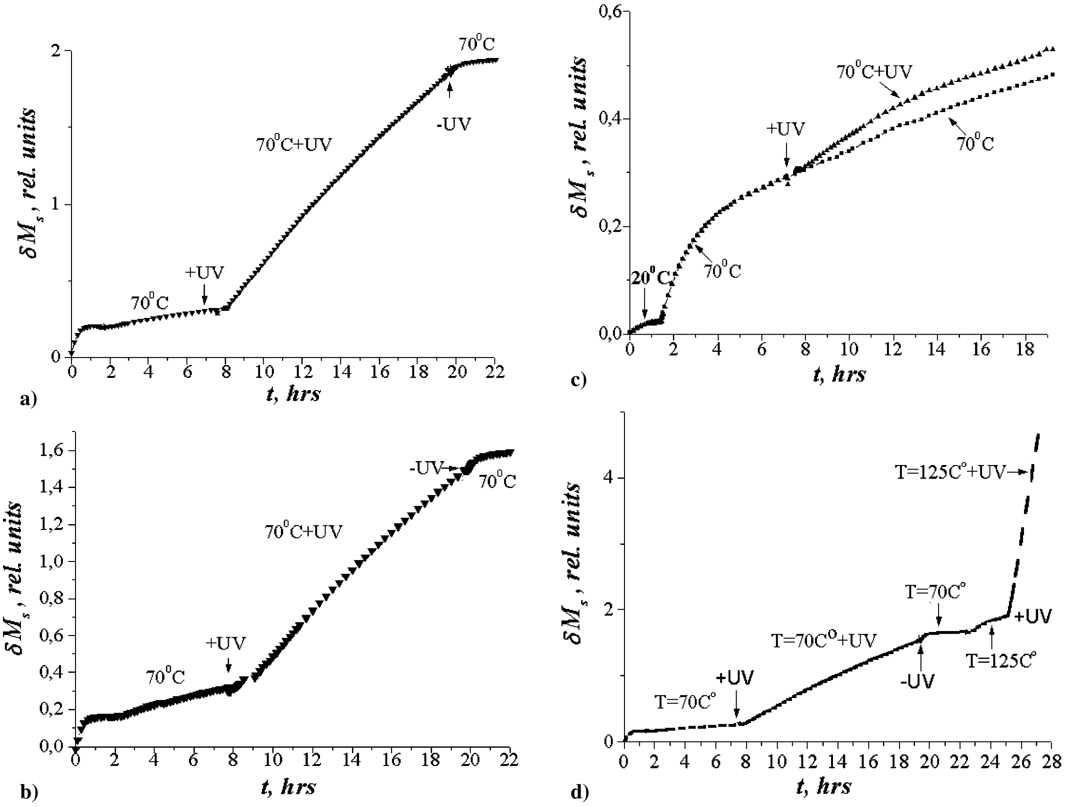

Fig. 4 Experimental curves of outgassing kinetics: a) and c) EKOM-1; b) model material with equal binder/filling agent volumes; and d) influence of actuation of UV source at *t* = 24 h on outgassing rate.

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